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Highly efficient fluorescent material

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Technical field

The invention proceeds from a fluorescent material from the class of the silicide nitrides in accordance with 10 the preamble of claim 1. In particular these are silicide nitrides which fluoresce in the yellow region.

Prior art

15 Fluorescent materials of the silicide nitride type such as Sr<sub>2</sub>Si<sub>3</sub>N<sub>6</sub> and Ba<sub>2</sub>Si<sub>3</sub>N<sub>6</sub>, already known from the article by Schlieper, Millus and Schlick: Nitridosilicate II, Hochtemperatursynthesen und Kristallstrukturen von Sr<sub>2</sub>Si<sub>3</sub>N<sub>6</sub> und Ba<sub>2</sub>Si<sub>3</sub>N<sub>6</sub> [Silicide nitrides II, high- 20 temperature syntheses and crystal structures of Sr<sub>2</sub>Si<sub>3</sub>N<sub>6</sub> and Ba<sub>2</sub>Si<sub>3</sub>N<sub>6</sub>], Z. anorg. allg. Chem. 621, (1995), page 1380. However, in this case no activators are specified which would suggest efficient emission in specific regions of the visible spectrum.

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Summary of the invention

It is an object of the present invention to provide a fluorescent material in accordance with the preamble of 30 claim 1, the efficiency of which is as high as possible, and which can be effectively stimulated by UV radiation in the region of 370 to 430 nm.

This object is achieved by the characterizing features 35 of claim 1. Particularly advantageous embodiments are to be found in the dependent claims.

There is as yet no yellow-emitting fluorescent material of high efficiency which can be effectively stimulated

in the region around 400 nm. The well known, normally used fluorescent material YAG:Ce can admittedly be effectively stimulated below 370 nm and above 430 nm, but not in the region around 400 nm. Other Ce-doped 5 garnets also exhibit only a slight ability to be stimulated in the range of use in question. It was therefore necessary to develop a completely different system.

10 According to the invention, the composition of the fluorescent material is selected such that it constitutes an Sr silicide nitride that is activated with trivalent Ce. The previously unknown fluorescent material  $\text{Sr}_2\text{Si}_5\text{N}_6:\text{Ce}^{3+}$  absorbs efficiently in the near 15 UV, in particular in the region of 370 to 430 nm, and has an efficient yellow luminescence. It is preferably activated by 1 to 10 mol% Ce (for Sr). In this case, the Sr can be replaced partially (advantageously up to at most 30 mol%) by Ba and/or Ca. A further embodiment 20 constitutes a silicide nitride of the type  $\text{SrSi}_3\text{N}_6:\text{Ce}^{3+}$ . In this case, too, the Sr can be replaced partially by Ba and/or Ca.

This fluorescent material is particularly well suited 25 as a yellow component for stimulation by a primary UV radiation source such as, for example, a UV LED, or else a lamp. It is possible thereby to implement a light source emitting ... .

30 ~~systems, as described similarly in WO 96/39877. A yellow-emitting light source is based on a LED primarily emitting UV radiation whose radiation is converted entirely into yellow light by a fluorescent material according to the invention.~~

35 In particular, this fluorescent material can be used in conjunction with a UV-LED (for example of the type InGaN), which generates white light by means of fluorescent materials emitting in the blue and yellow regions. Candidates for the blue component are known

per se; for example, BaMgAl<sub>10</sub>O<sub>17</sub>:Eu<sup>+</sup> (known as BAM) or Ba<sub>2</sub>SiO<sub>4</sub>(Cl,Br)<sub>2</sub>:Eu<sup>+</sup> or CaLa<sub>2</sub>S<sub>4</sub>Ce<sup>2+</sup> or else (Sr,Ba,Ca)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Eu<sup>+</sup> (known as SCAP). A red fluorescent material can be used, in addition, in order  
5 to improve the color of this system. (Y,La,Gd,Lu)<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>, SrS:Eu<sup>3+</sup> or else Sr<sub>2</sub>SiN<sub>3</sub>:Eu<sup>3+</sup> (not yet published, see EP-A 99 120 747.0) are particularly suitable.

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### Figures

The aim below is to explain the invention in more detail with the aid of two exemplary embodiments. In the drawing:

- 15 Figure 1 shows an emission spectrum of a first silicide nitride;  
Figure 2 shows the reflection spectrum of this silicide nitride;  
Figure 3 shows an emission spectrum of a second silicide nitride;  
20 Figure 4 shows the reflection spectrum of this silicide nitride;  
Figure 5 shows a semiconductor component which serves as light source for white light; and  
25 Figure 6 shows an emission spectrum of a mixture of three fluorescent materials.

### Description of the drawing

- 30 A concrete example of the fluorescent material according to the invention is shown in Figure 1, which concerns the emission of the fluorescent material, Sr<sub>2</sub>SiN<sub>3</sub>:Ce<sup>2+</sup>, the Ce proportion amounting to 4 mol % of the lattice sites occupied by Sr. The emission maximum is at 545 nm, and the mean wavelength at 472 nm. The color locus is x=0.393; y=0.514. The stimulation is performed at 400 nm.  
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The production is performed in the usual way, the

starting materials  $\text{Sr}_3\text{N}_2$ ,  $\text{Si}_3\text{N}_4$  and  $\text{CeO}_2$  being mixed with one another, and the mixture subsequently being baked in a furnace over 5 hours in a reducing fashion under  $\text{N}_2$  and  $\text{H}_2$  at  $1400^\circ\text{C}$ .

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Figure 2 shows the diffuse reflection spectrum of this fluorescent material. It exhibits a pronounced minimum in the region of 370 to 440 nm, which thereby demonstrates a good ability to be stimulated in this 10 region.

A second example of the fluorescent material according to the invention is shown in figure 3, which concerns emission of the fluorescent material  $\text{Sr}_2\text{Si}_3\text{N}_4:\text{Ce}^+$ , the 15 Ce proportion amounting to 8 mol% of the lattice sites occupied by Sr. The emission maximum is at 554 nm, the mean wavelength at 579 nm. The color locus is  $x=0.414; y=0.514$ .

20 The production is performed in the above described way, the mixture being baked in the oven over 6 hours in a reducing fashion under  $\text{N}_2$  at  $1400^\circ\text{C}$ .

25 Figure 4 shows the diffuse reflection spectrum of this fluorescent material. It exhibits a pronounced minimum in the region of 370 to 440 nm, which therefore demonstrates a good ability to be stimulated in this region.

30 The design of a light source of white light is shown explicitly in figure 5. The light source is a semiconductor component with a chip 1 of type InGaN having a peak emission wavelength of, for example, 390 nm, which is embedded in an opaque basic housing 8 in the region of a cut-out 9. The chip 1 is connected via a bond wire 14 to a first terminal 11, and directly to a second electric terminal 12. The cut-out 9 is filled with a potting compound 5 which contains as main constituents an epoxy casting resin 6 and 30% by

weight, and fluorescent pigments 6 (less than 15% by weight). A first fluorescent material is the silicide nitride presented as a first exemplary embodiment, while the second is a fluorescent material emitting in  
5 the blue region, here  $\text{Ba}_2\text{SiO}_4(\text{Cl},\text{Br})_2:\text{Eu}^+$  in particular. The cut-out has a wall 17 which serves as reflector for the primary and secondary radiation of the chip 1 or the pigments 6. The combination of the blue and yellow secondary radiation mixes to produce white.

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In a further exemplary embodiment, a mixture of three fluorescent materials is used as fluorescent pigment. A first fluorescent material (1) is the yellow-emitting silicide nitride  $\text{Sr}_2\text{Si}_2\text{N}_3:\text{Ce}^+$  presented as the first  
15 exemplary embodiment, the second (2) is the blue-emitting fluorescent material of the abovementioned SCAP, and the third (3) is a red-emitting fluorescent material of type  $\text{Sr}_2\text{Si}_2\text{N}_3:\text{Eu}^+$ . Figure 6 shows the emission spectrum of such an LED  
20 with primary emission at 375 nm, the individual components of yellow (1), blue (2) and red (3) adding together to form an overall spectrum (G) which conveys a white color sensation of high quality. The associated color locus is  $x=0.333$  and  $y=0.331$ . The use of three  
25 components ensures a particularly good color rendition.